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- (21) Application No. 51062/77 (22) Filed 8 Dec. 1977
- (61) Patent of addition to No. 1503315 dated 18 April 1975
- (44) Complete Specification published 11 June 1980
- (51) INT CL<sup>3</sup> C22B 61/00
- (52) Index at acceptance

CIA 13 310 313 518 G12 G33 G34 G36 G57 M10 N34 N40 N4 VFI

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(54) THE REMOVAL OF ACTINIDE METALS FROM SOLUTION

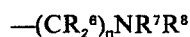
(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, EC2Y 9BU, a British Company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to the removal of actinide metals from solution. Accompanying the growth in nuclear chemistry there has been a corresponding increase in interest in removing actinide metals from solution. In particular the recovery of uranium from its natural surroundings, particularly by solution mining, has focussed interest on methods for removing it from solution. One such method is provided by the present invention.

According to the present invention there is provided a process for the removal of an actinide metal, as hereinafter defined, from solution which process comprises contacting the solution containing the actinide metal in the form of a soluble compound thereof with a substrate comprising the product obtained by reacting an inorganic solid containing surface hydroxyl groups with a compound of formula:



wherein Y is an —OR<sup>3</sup> group in which R<sup>3</sup> represents a hydrogen atom or an alkyl, aryl or acyl group containing up to 20 carbon atoms or Y is a halogen atom, X represents an —NR<sup>4</sup>R<sup>5</sup> group in which R<sup>4</sup> and R<sup>5</sup> which may be the same or different are hydrogen atoms or alkyl or aryl groups containing up to 20 carbon atoms or groups of formula:



in which R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> represent a H atom, an alkyl or aryl group containing up to 20 carbon atoms, n is an integer between 1 and 10 and wherein R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> may be the same or different or X is a saturated or unsaturated cyclic group in which one or more ring positions are occupied by nitrogen atoms, R is a divalent organic group containing up to 20 carbon atoms and R<sup>1</sup> and R<sup>2</sup>, which may be the same or different, are organic groups containing up to 20 carbon atoms or halogen atoms, under conditions which effect reaction between the group Y— and an —OH group on the surface of the inorganic solid thereby bonding the compound (I) to the inorganic solid.

The term actinide metal within the context of the present specification is defined as a metal with an atomic number equal to or greater than 89 in the Periodic Table of the elements. Thus the term actinide metal includes thorium, uranium and plutonium for example.

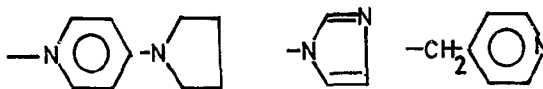
The inorganic solid containing surface hydroxyl groups may be alumina, titania, zirconia, glass, sepiolite, or a zeolitic molecular sieve. Preferably the inorganic solid is silica and more preferably silica gel. In addition mixtures of

inorganic solids may be used. Unless they have been subjected to severe treatments eg. heating above 1000°C all commercial silicas contain surface hydroxyl groups. However for the removal of metals from alkaline media, under which condition silica would be chemically attacked, it is preferred to employ an alkali resistant inorganic solid containing surface hydroxyl groups.

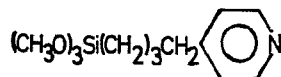
R<sup>1</sup> and R<sup>2</sup> in the compound of formula (I) may be alkyl, aryl, aryloxy or alkoxy groups or halogen atoms. Preferably R<sup>1</sup> and R<sup>2</sup> are halogen atoms, alkoxy or aryloxy groups. Preferably the group Y is an alkoxy group and the groups R<sup>1</sup> and R<sup>2</sup> and Y are identical alkoxy groups.

R in the compound of formula (I) is suitably an alkylene group containing up to 6 carbon atoms and is preferably a dimethylene group.

Examples of suitable groups X in the compound of formula (I) include —NH<sub>2</sub>, —NHR<sup>4</sup>, —NH(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>, —NR<sup>4</sup>(CH<sub>2</sub>)<sub>2</sub>NR<sup>7</sup>R<sup>8</sup>,

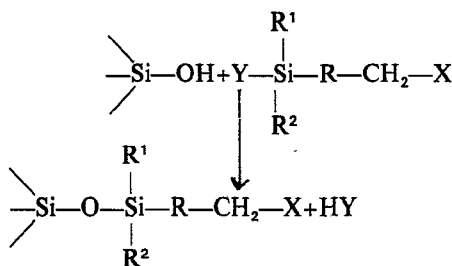


Examples of suitable compounds of formula (I) are (CH<sub>3</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>,



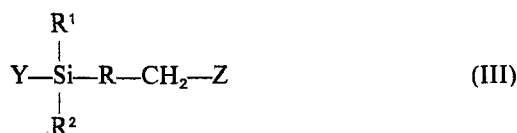
and (C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>.

In the case of silica the substrate is believed to be formed by the reaction represented by the following equation:

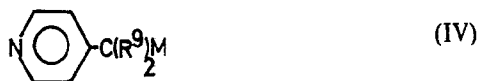


However the invention is not intended to be restricted in any way by the above equation representing the formation of the substrate.

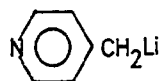
The substrate may be produced by reacting the inorganic solid containing surface hydroxyl groups with the compound of formula (I) in a single stage or in two or more stages. Thus in a single stage the reaction may be effected by warming the two together eg. under reflux in the presence of an inert solvent for the compound of formula (I) for 1 to 3 hours and thereafter separating the product. A suitable solvent for the compound of formula (I) is toluene. In two stages the substrate may be produced by reacting the inorganic solid containing surface hydroxyl groups with a compound of formula:



wherein Y, R, R<sup>1</sup> and R<sup>2</sup> have the same identity as in formula (I) above and Z is a halogen atom, preferably chlorine, in a first stage and in a second stage reacting the product from the first stage with a compound of formula:



wherein R<sup>a</sup> is a hydrogen atom or an alkyl group containing less than 20 carbon atoms, preferably less than 12 carbon atoms and M is an alkali metal, preferably lithium, and thereafter recovering the product from the second stage. Preferably the compound of formula (III) is (MeO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>Cl and the compound of formula (IV) is



Preferably the product from the first stage is treated to eliminate any remaining unreacted —OH groups on the surface of the inorganic solid by reaction with a silylating agent eg, hexamethyl disilazane, before reaction in the second stage. The treatment may be effected by refluxing for ½ to 2 hours and distilling off excess silylating agent.

The process of the invention is particularly applicable to the removal of the actinide metals, in the form of a soluble inorganic compound thereof from aqueous solutions but may also be used for their direct removal in the form of an organic compound thereof from non-aqueous solutions. Alternatively the process of the invention may be extended to aqueous solutions containing an actinide metal in a form other than a soluble inorganic compound thereof, for instance an organic compound or an inorganic compound insoluble in water, or as the elemental metal by converting the material to an inorganic compound soluble in water by a suitable pre-treatment.

The solution containing the metal in the form of a soluble compound thereof may be contacted with the substrate at any temperature in the range 0 to 200, preferably 20 to 100°C. Under atmospheric pressure the temperature will normally be in the range 0 to 100°C, for aqueous solutions, though if super atmospheric pressure is employed temperatures above 100°C may be used. For organic solutions the temperature may be in the range 0 to 200°C irrespective of the pressure.

The process of the invention is particularly advantageous for the removal of uranium from aqueous solution.

When the substrate loses its activity for removing metal it may either be disposed of without further treatment or the metal may be recovered therefrom by means known to those skilled in the art. One such method for removing the metal from the substrate is to contact the metal-loaded substrate with an aqueous solution followed by separation of the aqueous solution containing the metal from the substrate. The aqueous solution may be an aqueous solution of a mineral acid, such as hydrochloric or sulphuric acid. Alternatively the aqueous solution may be acidified brine or an aqueous solution of a metal salt, such as a nitrate or carbonate. Thereafter the metal may, if desired, be recovered from the aqueous solution.

The solution containing the metal may be contacted with the substrate batchwise, or, preferably, continuously by passing the solution over a bed of the substrate mounted in a suitable reactor.

The process of the invention is illustrated by the following Examples:

#### Example A

Reaction of N - aminoethylaminopropyltrimethoxysilane with silica

Acid washed U30 silica\* (20 g), which had been dried at 180°C, was stirred for 2 hours at room temperature with distilled water (10 ml) and toluene (250 ml). Residual water was distilled from the reaction flask and, after cooling to room temperature, the silane (MeO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (20 ml) was added. The mixture was stirred at reflux temperature for 3 hours during which time any alcohol produced was collected in a Dean & Stark tube which was periodically drained. After cooling, the silica product was transferred to a Soxhlet apparatus and extracted with dry methanol for 24 hours. The silica was finally dried in vacuo. On analysis the silica was found to contain 1.8 percent weight nitrogen.

#### Example B

Reaction of N - aminoethylaminopropyltrimethoxysilane with silica

Acid washed U30 silica\* (50 g), which had been dried at 180°C, was stirred at room temperature for 2 hours with distilled water (5 ml) and toluene (300 ml). To this mixture was added the silane (MeO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (12.5 ml)

and the stirring continued for a further 48 hours. The silica product was transferred to a Soxhlet apparatus and extracted with methanol for 16 hours prior to drying in vacuo. On analysis the silica was found to contain 2.1 percent weight nitrogen.

#### Example C

5 Reaction of  $\gamma$  - aminopropyltrimethoxysilane with silica 5

Acid washed U30 silica\* (25 g), which had been dried at 180°C, was stirred at room temperature for 2 hours with distilled water (15 ml) and toluene (300 ml). Residual water was distilled from the reaction flask and, after cooling to room temperature, the silane (EtO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (25 ml) was added. The mixture was stirred at reflux for 3 hours during which time any alcohol produced was collected in a Dean & Stark tube which was periodically drained. After cooling, the silica product was transferred to a Soxhlet apparatus and extracted with methanol for 24 hours prior to drying in vacuo. On analysis the silica was found to contain 0.7 percent weight nitrogen. 10

15 Examples A, B and C are not examples according to the invention. They are included for the purpose of demonstrating the production of substrates useful in the process of the invention. 15

#### Example 1

20 200 ml of a dilute sulphuric acid solution of uranyl sulphate containing 1.64 g UO<sub>2</sub>SO<sub>4</sub>·3H<sub>2</sub>O was stirred with 1.62 g of the diamine functionalised silica, prepared as described in Example B, for 5 hours at room temperature. After allowing the mixture to stand overnight the silica product was isolated by filtration and then Soxhlet extracted with water for 18 hours followed by methanol for 8 hours. The silica was finally dried in vacuo. On analysis the silica was found to contain 1.2 percent weight uranium, measured as uranium metal. 25

#### Example 2

200 ml of a dilute sulphuric acid solution of uranyl sulphate containing 2.19 g UO<sub>2</sub>SO<sub>4</sub>·3H<sub>2</sub>O was stirred with 1.92 g of the primary amine functionalised silica, prepared as described in Example C for 5 hours at room temperature. After allowing the mixture to stand overnight the silica product was transferred to a Soxhlet apparatus and extracted with water for 18 hours then methanol for 8 hours. The silica was finally dried in vacuo. On analysis the silica was found to contain 0.3 percent weight uranium, measured as uranium metal. 30

#### Comparison Test

35 200 ml of a dilute sulphuric acid solution of uranyl sulphate containing 1.29 g UO<sub>2</sub>SO<sub>4</sub>·3H<sub>2</sub>O was stirred with 2.11 g of acid washed U30 silica\* for 5 hours at room temperature. After allowing the mixture to stand for 18 hours the silica product was isolated by filtration and then Soxhlet extracted with water for 18 hours followed by methanol for 8 hours. The silica was finally dried in vacuo. On analysis the silica was found to contain 0.1 percent weight uranium, measured as uranium metal. 40

This is not an example according to the invention and is included only for the purpose of comparison.

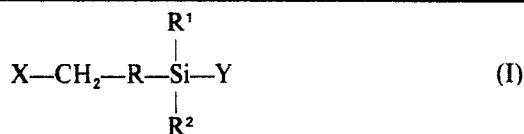
#### Example 3

45 250 ml of an aqueous solution of uranyl nitrate containing 0.66 g UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was stirred with 1.58 g of the diamine functionalised silica, prepared as described in Example A for 4 hours at room temperature. After allowing the mixture to stand for 65 hours the silica product was isolated by filtration and then Soxhlet extracted with water for 12 hours followed by methanol for 8 hours. The silica was finally dried in vacuo. On analysis the silica was found to contain 5.9 percent weight uranium, measured as uranium metal. 50

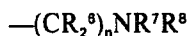
#### WHAT WE CLAIM IS:—

1. A process for the removal of an actinide metal, as hereinbefore defined, from solution which process comprises contacting the solution containing the actinide metal, in the form of a soluble compound thereof with a substrate comprising the product obtained by reacting an inorganic solid containing surface hydroxyl groups with a compound of formula: 55

\*U30 silica is supplied by J. Crosfield and Son, Warrington.



wherein Y is an  $-\text{OR}^3$  group in which  $\text{R}^3$  represents a hydrogen atom or an alkyl, aryl or acyl group containing up to 20 carbon atoms or Y is a halogen atom, X represents an  $-\text{NR}^4\text{R}^5$  group in which  $\text{R}^4$  and  $\text{R}^5$ , which may be the same or different, are hydrogen atoms or alkyl or aryl groups containing up to 20 carbon atoms or groups of formula:



in which  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  represent a H atom, an alkyl or aryl group containing up to 20 carbon atoms, n is an integer between 1 and 10 and wherein  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  may be the same or different or X is a saturated or unsaturated cyclic group in which one or more ring positions are occupied by nitrogen atoms, R is a divalent organic group containing up to 20 carbon atoms and  $\text{R}^1$  and  $\text{R}^2$  which may be the same or different, are organic groups containing up to 20 carbon atoms or halogen atoms, under conditions which effect reaction between the group Y— and an  $-\text{OH}$  group on the surface of the inorganic solid thereby bonding the compound (I) to the inorganic solid.

2. A process according to claim 1 wherein the inorganic solid is alumina, titania, zirconia, glass, sepiolite or a zeolitic molecular sieve.

3. A process according to claim 2 wherein the inorganic solid is silica.

4. A process according to claim 3 wherein the inorganic solid is silica gel.

5. A process according to any one of the preceding claims wherein  $\text{R}^1$  and  $\text{R}^2$  in the compound of formula (I) are alkyl, aryl, aryloxy or alkoxy groups or halogen atoms.

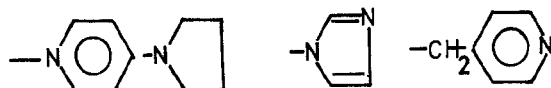
6. A process according to claim 5 wherein  $\text{R}^1$  and  $\text{R}^2$  are halogen atoms, alkoxy or aryloxy groups.

7. A process according to any one of the previous claims wherein the group Y in the compound of formula (I) is an alkoxy group and the groups Y,  $\text{R}^1$  and  $\text{R}^2$  are identical alkoxy groups.

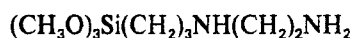
8. A process according to any one of the preceding claims wherein R in the compound of formula (I) is an alkylene group containing up to 6 carbon atoms.

9. A process according to claim 8 wherein the alkylene group is a dimethylene group.

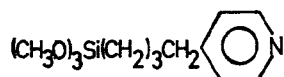
10. A process according to any one of the preceding claims wherein the group X in the compound of formula (I) is  $-\text{NH}_2$ ,  $-\text{NHR}^4$ ,  $-\text{NH}(\text{CH}_2)_2\text{NH}_2$ ,  $-\text{NR}^4(\text{CH}_2)_2\text{NR}^5$ ,



11. A process according to any one of the preceding claims wherein the compound of formula (I) is:



12. A process according to any one of claims 1 to 10 wherein the compound of formula (I) is

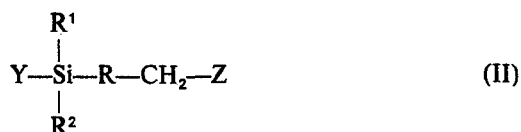


13. A process according to any one of claims 1 to 10 wherein the compound of formula (I) is  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ .

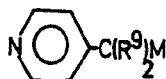
14. A process according to any one of the preceding claims wherein the substrate is produced in a single stage by warming the inorganic solid containing surface hydroxyl groups with the compound of formula (I) in the presence of an inert solvent for the compound of formula (I) for 1 to 3 hours and thereafter separating the product.

15. A process according to claim 14 wherein the inert solvent is toluene.

16. A process according to any one of claims 1 to 13 wherein the substrate is produced in two stages by reacting the inorganic solid containing surface hydroxyl groups in a first stage with a compound of formula:—



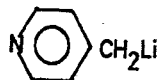
5 wherein Y, R, R<sup>1</sup> and R<sup>2</sup> have the same identity as in the formula (I) and Z is a halogen atom, and in a second stage reacting the product from the first stage with a compound of formula:—



10 wherein R<sup>9</sup> is a hydrogen atom or an alkyl group containing less than 12 carbon atoms and M is an alkali metal, and thereafter recovering the product from the second stage.

17. A process according to claim 16 wherein the alkali metal in the formula (III) is lithium and Z in the formula (II) is a chlorine atom.

15 18. A process according to either one of claims 16 and 17 wherein the compound of formula (II) is (MeO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>Cl and the compound of formula (III) is



20 19. A process according to any one of claims 16 to 18 wherein the product from the first stage is treated to eliminate any remaining unreacted —OH groups on the surface of the inorganic solid by reaction with a silylating agent before reaction in the second stage.

20. A process according to any one of the preceding claims wherein the solution containing the metal in the form of a soluble compound thereof is contacted with the substrate at a temperature in the range from 0 to 200°C.

25 21. A process according to claim 20 wherein the solution is an aqueous solution and the temperature is in the range 20 to 100°C at atmospheric pressure.

22. A process according to any one of the preceding claims wherein uranium is removed from an aqueous solution thereof.

30 23. A process according to any one of the previous claims wherein the actinide metal is recovered from the substrate.

24. A process for the removal of uranium from solution substantially as hereinbefore described with reference to Examples 1 to 3.

25. An actinide metal whenever removed from solution by a process as claimed in any one of the preceding claims.

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